

# Soft X-ray Spectroscopic Study of $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$

J.-H. Guo<sup>1</sup>, L. Norin<sup>2</sup>, L. Qian<sup>1</sup>, C. S  the<sup>1</sup>, A. Agui<sup>1</sup>, U. Jansson<sup>2</sup>, and J. Nordgren<sup>1</sup>

<sup>1</sup>Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

<sup>2</sup>Department of Inorganic Chemistry, Uppsala University, Box 538, S-751 21 Uppsala, Sweden

## INTRODUCTION

$\text{C}_{60}$  reacts with alkali and alkaline earth metals to form ionic intercalation compounds or fullerides. Very few reports have been published on the formation of fullerides based on transition metals and  $\text{C}_{60}$ . This can be due to the fact that such compounds may be thermodynamically unstable and separate into bulk metal and pure  $\text{C}_{60}$ . In a recent study, however, it was suggested that a  $\text{Ti}_x\text{C}_{60}$  compound could be synthesized by co-evaporation of Ti and  $\text{C}_{60}$  [1]. This was also confirmed by soft x-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) [2].

In the present study we have used XES and XAS to study the oxidized low Ti-content  $\text{C}_{60}$  film. This may be a useful method to learn about the origin of these titanium fulleride compounds, as XES has a few particularly interesting properties. Firstly, it allows direct probing of the site and element specific angular momentum components of the density of states (DOS), and, secondly, it provides bulk information owing to the relatively large probing depth.

## EXPERIMENTAL

The  $\text{Ti}_x\text{C}_{60}$  film was made by co-evaporation of  $\text{C}_{60}$  and Ti from a Knudsen-type effusion cell and an e-beam evaporator, respectively. The reference film  $\text{C}_{60}$  was made at the same conditions without Ti evaporation. The films were deposited on Si(100) substrates in a UHV deposition chamber with a base pressure of  $5 \times 10^{-10}$  Torr [1]. After oxidation the composition of the sample was determined to  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$  by XPS.

The experiments were performed at beamline 7.0 at ALS, LBNL. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [3]. XAS spectra were obtained by measuring the total electron yield from the sample current. The resolution of the monochromator was set to 0.20, 0.40 and 0.80 eV, respectively, for the C  $1s$ , Ti  $2p$  and O  $1s$  absorption edges. The XAS spectra were normalized by means of the photocurrent from a clean gold mesh in front of the sample to correct for intensity fluctuations in the photon beam. The XES spectra were recorded using a high-resolution grazing-incidence grating spectrometer [4]. During the x-ray emission measurements, the resolution of the beamline was the same as in the XAS measurements, and the resolution of the grating spectrometer was set at 0.5 eV, 0.7 and 1.0 eV, respectively, for C  $K\alpha$ , Ti  $L$  and O  $K\alpha$  emission spectra.

## RESULTS AND DISCUSSION

Figure 1 displays the C  $1s$  absorption spectra of  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$ , pure  $\text{C}_{60}$  and  $\text{TiC}_{0.61}$ . The  $\text{C}_{60}$  XAS spectrum presents four  $\pi^*$  resonances with the lowest unoccupied molecular orbital (LUMO) located at 284.5 eV and many discrete absorption features (multi-electron excitations) superimposed on a shape resonance in the near-continuum part. The relevant  $\pi^*$  unoccupied molecular orbitals governing the XAS spectrum were found to be of  $t_{1u}$  ( $A_1$ ),  $t_{1g}$  ( $A_2$ ),  $t_{2u}+h_g$  ( $A_3$ ),  $h_u+a_g+g_g$  ( $A_4$ ) symmetries [5].

The C  $1s$  absorption spectrum of Ti doped thin film shows less prominent  $\pi^*$  resonances as compared to  $C_{60}$  fullerene. The absorption peaks corresponding to  $A_3$  and  $A_4$  for  $C_{60}$  are visible in  $Ti_{2.2}O_{5.9}C_{60}$  with less intensity and broader linewidth. The reduced peak height of the LUMO peak may indicate a charge transfer towards to the  $C_{60}$  molecule. The absorption peaks in the upper conduction band ( $\sigma^*$ ) are less resolved in the  $Ti_{2.2}O_{5.9}C_{60}$  film. The C  $1s$  absorption of  $TiC_{0.61}$  shows a broader  $\pi^*$  resonance at 285.2 eV and a  $\sigma^*$  resonance centered at 292 eV.

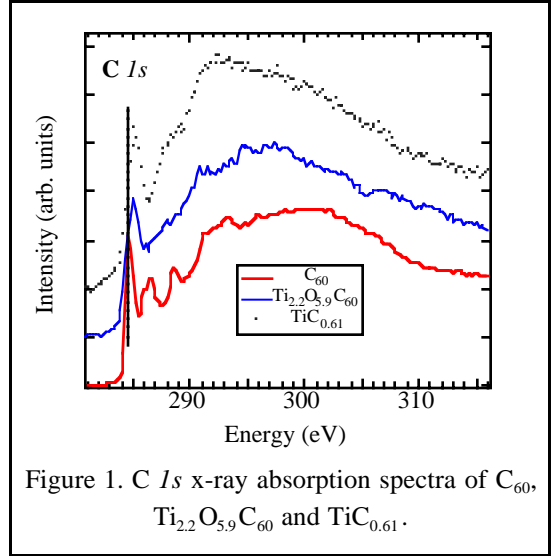


Figure 1. C  $1s$  x-ray absorption spectra of  $C_{60}$ ,  $Ti_{2.2}O_{5.9}C_{60}$  and  $TiC_{0.61}$ .

Figure 2 shows O  $1s$  XAS spectra of  $Ti_{2.2}O_{5.9}C_{60}$  and a reference  $TiO_2$  sample. As one can see, the spectra are divided into two regions below and above the ionization threshold ( $\sim 536$  eV), respectively. The first region is attributed to oxygen  $2p$ , weight-hybridized in states of predominantly Ti  $3d$  character [6, 7]. The second region, above the threshold, is attributed to oxygen  $p$  character hybridized with Ti  $4s$  and  $4p$  states [8]. It is concluded that the large-energy spread (some 15 eV above  $E_F$ ) of oxygen  $2p$  states is an indication of strong covalency in the  $TiO_2$  compound.

In a purely ionic model, oxygen has a configuration of  $O 1s^2 2s^2 2p^6$  and the  $1s \rightarrow 2p$  channel would be closed in XAS. Covalency reduces the number of filled states with O  $2p$  character, so that the strength of the O  $1s$  signal at the threshold is related to the degree of covalency [9]. The decrease in intensity of the first-region bands, relative to the second-region bands is consistent with the observation in a O  $1s$  XAS study going across the transition-metal series [6]. The main reason for this was the decrease in number of unoccupied  $3d$  states available for mixing with O  $2p$  states. In the O  $1s$  absorption of  $Ti_{2.2}O_{5.9}C_{60}$ , the decrease in intensity of the first band may be caused by the interaction between Ti  $3d$  and C  $2p$  from  $C_{60}$ .

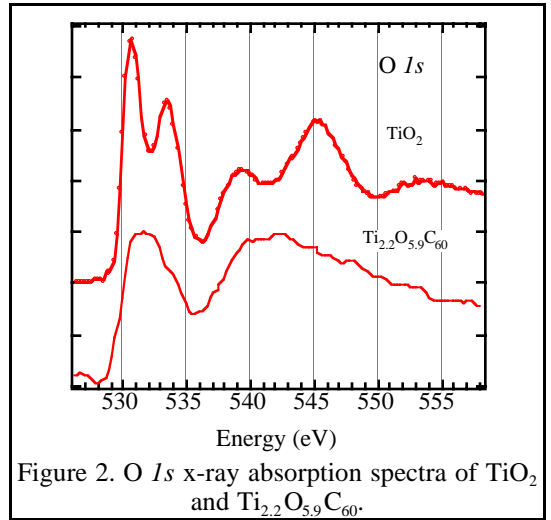


Figure 2. O  $1s$  x-ray absorption spectra of  $TiO_2$  and  $Ti_{2.2}O_{5.9}C_{60}$ .

At the Ti  $2p$  edge of  $TiO_2$ , the absorption spectrum contains four dominant peaks (Fig. 3). The first and second peaks are related to respectively the  $t_{2g}$  and  $e_g$  symmetries of the  $L_3$  edge with an energy splitting of some 2.0 eV. The third and fourth peaks are related to respectively the  $t_{2g}$  and  $e_g$  symmetries of the  $L_2$  edge [10]. Below the first absorption peak (at 456.7 eV) there are small leading structures that are related to a transition which is forbidden in LS-coupling, but it becomes allowed because of the multiplet  $p-d$  interactions.

In the Ti  $2p$  absorption spectrum of  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$ , the absorption peaks are shifted towards low-energy, and the energy splitting (about 1.5 eV) and intensity ratio between  $t_{2g}$  and  $e_g$  become less as compared to  $\text{TiO}_2$ . The experimental observations can be explained as a superposition of two different titanium sites with the  $3d^1$  and  $3d^0$  configurations. In the x-ray absorption study of  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$  perovskites [11], it was demonstrated that the metal (Ti)  $2p$  x-ray absorption spectra of the  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ -series can be described as a superposition of  $x$  times the spectrum of  $\text{SrTiO}_3$  ( $3d^0$  configuration) plus  $1-x$  times the spectrum of  $\text{LaTiO}_3$  ( $3d^1$  configuration).

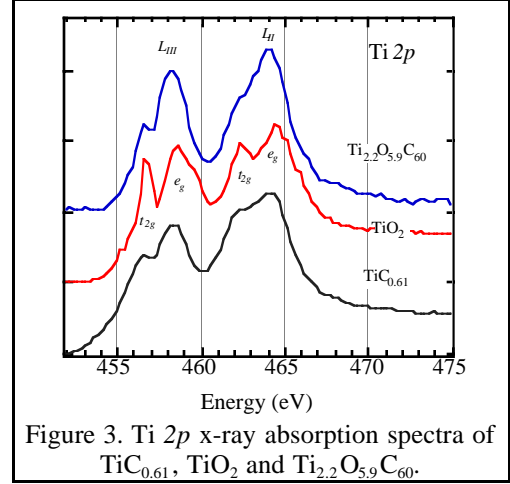


Figure 3. Ti  $2p$  x-ray absorption spectra of  $\text{TiC}_{0.61}$ ,  $\text{TiO}_2$  and  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$ .

The resonant and non-resonant C  $K\alpha$  XES spectra of  $\text{C}_{60}$ ,  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$ , and  $\text{TiC}_{0.61}$  are presented in Figure 4. The resonant C  $K\alpha$  emission of  $\text{C}_{60}$  contains five resolved features, labelled  $E_1$ ,  $E_2$ ,  $E_3$ ,  $E_4$  and  $E_5$ . The sharp peak at 284.5 eV is the recombination peak which has the same energy as the incoming photons. According to *ab initio* Hartree-Fock calculations [12, 13] the first emission band  $E_1$  corresponds to the highest occupied molecular orbital (HOMO) with  $4h_u$  symmetry, while the second band  $E_2$  represents a combination of the nearly degenerate  $4g_g$  and  $7h_g$  orbitals. The bands  $E_3$  and  $E_4$  contain more complicated molecular orbital combinations. The band  $E_5$  contains the  $2h_u$ ,  $3t_{1u}$  and  $2g_g$  orbitals. A strong excitation dependence for all these features can clearly be discerned as comparing the resonant and non-resonant x-ray emission spectra in Figure 4.

The C  $K\alpha$  emission spectrum of the  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$  film is similar to pristine  $\text{C}_{60}$  regarding the total emission bandwidth, peak energy positions and intensity ratio of different emission bands. On the other hand, the C  $K\alpha$  emission spectrum of  $\text{TiC}_{0.61}$  exhibits a single-band structure with much smaller bandwidth for both resonant and non-resonant excitations. This is a clear evidence that the buckyball structure is preserved in  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$ . The small difference reflects the influence on the electronic structure of the  $\text{C}_{60}$  molecule by the presence of titanium and oxygen atoms.

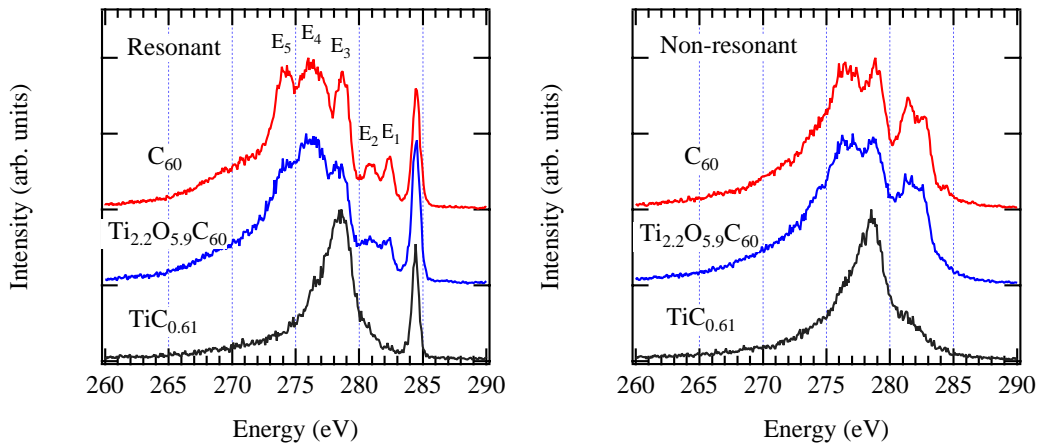


Figure 4. C  $K\alpha$  x-ray emission spectra of  $\text{C}_{60}$ ,  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$  and  $\text{TiC}_{0.61}$ .

Figure 5 shows the O  $K\alpha$  emission spectra of  $\text{TiO}_2$  and  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$  with resonant and non-resonant photon excitations. Basically, all four spectra exhibit two sub-band structures. In the resonant case, the splitting between the two sub-bands is 3.2 eV in  $\text{TiO}_2$  and only 2 eV in  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$ . The full width at half maximum (FWHM) and the intensity of the low-energy peak of the O  $K\alpha$  spectra vary with the energy of the incoming photons as shown in Figure 5. Due to strong Ti  $3d$  - O  $2p$  hybridization, the occupied O  $2p$  states form a wide band, split into bonding and anti-bonding sub-bands [14]. The lower energy splitting of the sub-bands in  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$  in Fig. 5 may be caused by the chemical interaction between Ti and  $\text{C}_{60}$ .

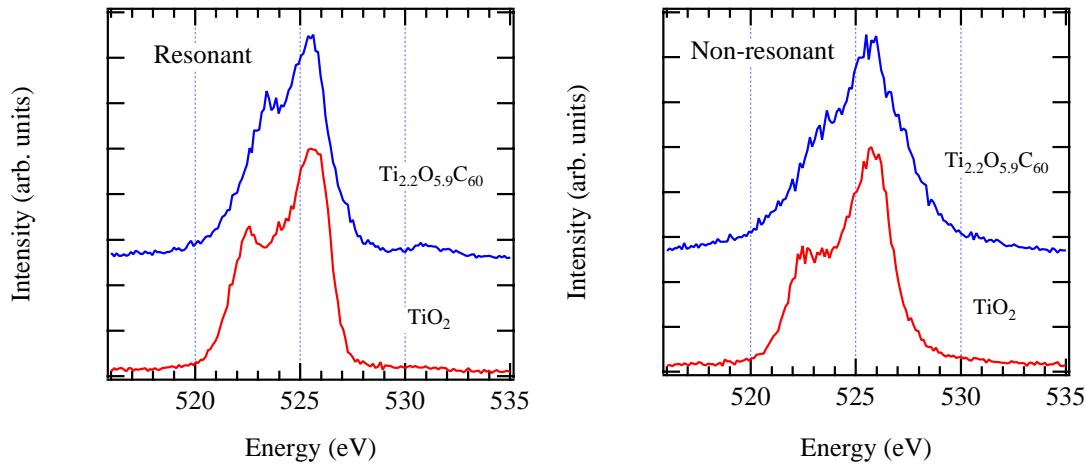


Figure 5. O  $K\alpha$  x-ray emission spectra of  $\text{Ti}_{2.2}\text{O}_{5.9}\text{C}_{60}$  and  $\text{TiO}_2$ .

## REFERENCES

- [1] L. Norin, *et al.*, Chem. Mater. **10**, 1184 (1998).
- [2] L. Qian, *et al.*, submitted to Phys. Rev. B.
- [3] T. Warwick, *et al.*, Rev. Sci. Instr. **66**, 2037 (1995).
- [4] J. Nordgren, *et al.*, Rev. Sci. Instr. **60**, 1690 (1989).
- [5] J.-H. Guo, *et al.*, Phys. Rev. B **52**, 10681 (1995).
- [6] F. M. F. de Groot, *et al.*, Phys. Rev. B **40**, 5715 (1989).
- [7] D.W. Fisher, J. Phys. Chem. Solids **32**, 2455 (1971).
- [8] This doesn't agree with, e.g. P. R. Sarade, J. Phys. F **17**, 1605 (1987).
- [9] M. Pedio, *et al.*, Phys. Rev. B **40**, 7924 (1989).
- [10] F. M. F. de Groot, *et al.*, Physics and Chemistry of Minerals **19**, 140 (1992).
- [11] F. M. F. de Groot, *et al.*, Phys. Rev. B **40**, 5715 (1989).
- [12] J.-H. Guo, *et al.*, Chem. Phys. Lett. **227**, 98 (1994).
- [13] Y. Luo, *et al.*, Phys. Rev. B **52**, 14479 (1995).
- [14] J. Yu, S. Massida, and A. Freeman, Physica C **152**, 273 (1988).
- [15] J.-E. Rubensson, *et al.*, ALS Compendium, 161 (1997).

This work was supported by the Swedish Natural Science Research Council and the G. Gustafsson Foundation for Science and Medicine.

Principal investigator: E. Joseph Nordgren, Department of Physics, Uppsala University. E-mail: joseph@fysik.uu.se. Telephone: +46 18 4713554.